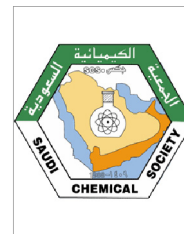




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ORIGINAL ARTICLE

Novel fluorescent pH sensor based on 5-(4-carboxy-phenyl)-10,15,20-tris(phenyl)-porphyrin



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Received 13 October 2013; accepted 8 October 2014

Available online 17 October 2014

KEYWORDS

Functionalized porphyrin;
Fluorescence;
pH Sensor;
Acid media;
UV–vis

Abstract A novel fluorescent pH sensor based on 5-(4-carboxy-phenyl)-10,15,20-tris(phenyl)-porphyrin, as sensing agent, has been developed. The carboxyl functionalized asymmetric porphyrin has been synthesized and characterized by high performance liquid chromatography (HPLC), thin layer chromatography (TLC), proton nuclear magnetic resonance (¹H NMR), Fourier transform infrared spectroscopy (FT-IR), ultraviolet–visible (UV–vis), emission, excitation and mass spectrometry (MS) spectra. Optical and fluorescence behaviors were investigated in relationship with variation of acid concentration in the range of acid pH from 1.5 to 5.5. Upon increasing the acidity of the solution, the decrease of the fluorescence intensity was noticed, as a linear function of pH. Different metal ions were tested to put into evidence the changes regarding the fluorescence intensity, but the fluorescence obtained results revealed no significant interference on pH determination. The conclusion is that the proposed fluorescent sensor can measure pH in acid range in the presence of different metal ions making this sensor a proper one for pH determinations in leaching solutions of the recyclable processes of valuable metals.

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Peer review under responsibility of King Saud University.



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1. Introduction

In the last decade, many amazing reports focused on applications of functional nanomaterials based on porphyrin for information storage (Lindsey et al., 2011), induced luminescence (Liu et al., 2008) photocatalysis (Cai et al., 2009; Yao et al., 2012) sensors (Lvova et al., 2013; Vlascici et al., 2005; Vlascici et al., 2012) and multisensor approach (known as electronic tongue (ET) systems) (Paolesse et al., 2008; Lvova et al.,

2006) and also on hybrid porous materials with enhanced optical properties (Fagadar-Cosma et al., 2009a,b; Dudas et al., 2010) able for gas sensing (Çaycı et al., 2011; Popescu et al., 2011) and gas storage (Oztek et al., 2011). Highly sophisticated materials explored the potential applications of porphyrin derivatives for diagnosis (Spagnul et al., 2013) and noninvasive treatment of cancer (PDT) (Wang et al., 2012; Senge and Radomski, 2013).

Due to its high selectivity and sensitivity, fluorescence method has gained much interest for the detection and quantitative determination of heavy metals (Delmarre et al., 1999). Huge amount of work was done to use porphyrins as sensing elements for optochemical sensors immobilized in organic or inorganic matrices. The reaction between the analyte and the sensitive dye will produce changes regarding the absorption or fluorescence behavior of the sensitive molecule. The use of 5,10,15,20-tetra(*p*-sulfonatophenyl)porphyrin as fluorescence indicator generated a highly sensitive device for mercury detection (Plaschke et al., 1995). Heavy metal cations such as: Fe^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} quenched the emission of *meso*-tetra(4-*N,N,N*-trimethylanilinium)porphyrin-Pd, demonstrating its capability to detect these ions in water samples, with wide linear range, low detection limits and good precision (Hu et al., 2009). A new optical sensor for sensing of Pb^{2+} by using 5,10,15,20-tetra(3-bromo-4-hydroxyphenyl)porphyrin was also developed (Bozkurt et al., 2009).

Based on our previous work that put into evidence the capacity of a water soluble metalloporphyrin, 5,10,15,20-tetrakis(*N*-methyl-4-pyridyl)porphyrin-Zn(II)tetrachloride, to act as an optical pH sensor in the 5.5–10.5 domain (Fagadar-Cosma et al., 2011), the present study explored the potential application of an asymmetrical A_3B porphyrin for realizing a fluorescent sensor for pH measurements. An asymmetrical A_3B porphyrin can be usually obtained by a multicomponent reaction between pyrrole and two different substituted aldehydes and is containing three substituted phenyl rings derived from one aldehyde and one substituted phenyl ring derived from the other.

Because less attention was paid on the fluorescent amphiphilic compounds which are pH sensitive in the lower pH region ($\text{pH} < 4$) (Tian et al., 2012) much attention must be given to synthetic methods (Fagadar-Cosma et al., 2007a, 2012) in order to obtain A_3B differentially functionalized porphyrins exhibiting the required properties.

The need for monitoring the pH levels of strongly acidic media sprung from the knowledge that such media are found in the human body or in industrial used waters.

Besides, many chemical and biological processes occur in acid water environment and might involve significant pH changes. Medical monitoring of the pH in acidic media is a must regarding the study of strongly acidic medium which exists in the human stomach or with respect to acidic lysosomes and endosomes in living cells (Vasylevska et al., 2007) or in cancerous tissues (Fagadar-Cosma et al., 2007a).

Although the glass electrode is recommended as the preferred tool for pH measurements, this approach suffers from many drawbacks: it is invasive and might create the risk of electric shock during *in vivo* measurements (Callan et al., 2005).

Fluorescent pH sensors, based on more hydrophobic dyes are the best alternative for *in situ* applications due to strong limitations of leaching and to the huge potential to be

improved by covalent immobilization of the dye into a solid matrix permeable to protons (Ferrari et al., 2013), such as: a hybrid sol–gel silica nanomaterial (Fagadar-Cosma et al., 2014) or an appropriate polymeric membrane.

In order to tune the solubility, chemical recognition and aggregation, the so-called amphiphilic porphyrin molecules have been synthesized, since the porphyrin ring is hydrophobic, but it is possible to substitute the phenyl rings with polar groups.

Porphyrins *meso*-phenyl substituted with carboxy-functional groups have been reported (Bakar et al., 2009) as efficient *second generation photosensitizers* for PDT (having the capacity to absorb at long wavelength in the red region of the visible spectrum; $\lambda > 630 \text{ nm}$). Besides, they can both alter the amphiphilicity of the macrocycle and exhibit specific chemical interactions that recommend them to be used as building blocks.

A previous paper (Amao et al., 1999) reported the quenching of palladium tetrakis(4-carboxy-phenyl)porphyrin self-assembled membrane on an alumina plate with the increase of oxygen concentration, proving that this membrane is a highly sensitive device for oxygen concentration.

In order to achieve the goal of developing a novel chemosensor for pH sensing in acid media, 5-(4-carboxy-phenyl)-10,15,20-tris(phenyl)-porphyrin (Fig. 1) was obtained by using the Lindsey method (Lindsey and Wagner, 1989; Lindsey et al., 1987) for preparation of 4-(methoxycarbonyl)phenyltriphenylporphyrin, followed by hydrolysis of ester-type porphyrin (Matsumoto et al., 2008).

2. Material and methods

2.1. Chemicals

Reagents *p.a.* grade: benzaldehyde, *p*-methoxy-carbonylbenzaldehyde, pyrrole, $\text{BF}_3\cdot\text{OEt}_2$, THF, CH_2Cl_2 , hexane, EtOH, EtOAc and hydrochloric acid 1 M, purchased from Fluka, Merck and Sigma–Aldrich, were used as received. The solutions for the selectivity measurements were prepared using the chloride salts of the given cations (Merck, Darmstadt, Germany). All aqueous solutions were prepared with distilled water. Thin-layer chromatography (TLC) was performed using Merck 60 F254 silica gel. Silica gel 60 (70–230 mesh,

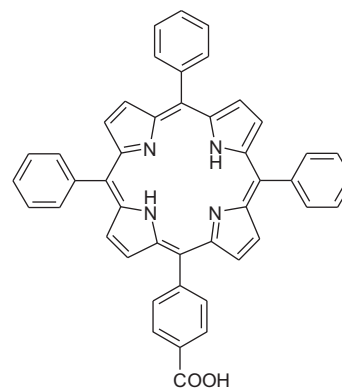


Figure 1 The structure of 5-(4-carboxy-phenyl)-10,15,20-tris(phenyl)-porphyrin.

Merck) was used for column chromatography. The pH values were verified with buffer solutions provided from Sigma-Aldrich: pH = 4.65 (sodium acetate/acetic acid), pH = 4 (potassium hydrogen phthalate/formaldehyde) and pH = 2.06 (HCl/KCl).

2.2. Apparatus

UV-visible spectra were recorded on a UV/VIS PERKIN ELMER, LAMBDA 12 spectrometer and on a JASCO UV-visible spectrometer, V-650 model. The photoemission and photoexcitation spectra were recorded in THF/distilled water: 1/1 (v/v) with the help of a Perkin Elmer LS55 luminescence spectrometer. FT-IR spectra were registered as KBr pellets on a Jasco 430 instrument in the 4000–400 cm^{-1} range. Thin-layer chromatography (TLC) was performed on silica gel plate 60 F254 pre-coated aluminum sheets from Merck. The HPLC analysis was performed on a JASCO apparatus equipped with a silica gel KROMASIL 100 SIL 5 μm 250 \times 4.0 mm column and a MD 1510 detector, at ambient temperature, using UV detection at 417 nm. ^1H NMR spectra were registered in CDCl_3 on a Bruker DRX 400 apparatus at 400 MHz. Proton chemical shifts, expressed in δ (ppm), were internally referenced to the residual proton resonance in CDCl_3 (δ 7.26). A Bruker esquire HCT series mass spectrometer with Atmospheric Pressure Interface–Electrospray Ionization was used for registering MS. The pH values of the solutions were measured with a PH60 EXTECH pH-meter.

2.3. Spectroscopic studies

Absorption and fluorescence spectra were recorded using 1 cm path length cells, at ambient temperature. The luminescence spectra were recorded at 100 nm/min rate with constant slit widths: 3 nm for excitation and respectively, 3.4 nm for emission. A 515 nm cut-off filter, to eliminate harmonic or scattering peaks, was used. For introducing acidic conditions, standard solutions of 1 M HCl were used. The concentration of 5-(4-carboxy-phenyl)-10,15,20-tris(phenyl)-porphyrin was kept constant in all measurements.

2.4. Preparation of 5-(4-carboxy-phenyl)-10,15,20-tris(phenyl)-porphyrin

Preparation of 5-(4-carboxy-phenyl)-10,15,20-tris(phenyl)-porphyrin was performed using the multicomponent modified Lindsey method to obtain 5-(4-methoxycarbonyl-phenyl)-10,15,20-tris(phenyl)-porphyrin (Lvova et al., 2006, 2013; Oztek et al., 2011; Paolesse et al., 2008; Plaschke et al., 1995) which was transformed via base-hydrolysis using NaOH–EtOH (Bakar et al., 2009) into the desired carboxy-phenyl substituted porphyrin. Chromatography on column of silica gel, eluted with $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ = 3/1 was used for separation, followed by evaporation of the solvent to gave a dark-purple solid.

2.5. 5-(4-Carboxy-phenyl)-10,15,20-tris(phenyl)-porphyrin

Dark purple solid; yield: 11.3%; mp over 300 $^\circ\text{C}$; FT-IR (KBr) (ν , cm^{-1}): 3443.28 (ν N–H), 3054.69 (ν C–H_{Ph}); 1686.44 (ν

C=O), 1603.52 and 1558.2 (ν C=C_{Ph}), 1470.46 (ν C=C_{Ph}); 1419.35 (ν COO); 1348.0 (ν C–N); 1279.54 (ν C–O–H); 1179.26 (δ C–H_{Ph}), 1073.19 (δ C–H_{pyrrol}); 964.23 (δ C–H_{pyrrol}); 797.42 (γ C–H_{pyrrol}); 725.10 (γ C–H_{Ph}); 700.99 (γ C–H_{Ph}); ^1H NMR (CDCl_3), ppm: 8.91 (d, 2H, β -pyrrole), 8.84 (bs, 4H, β -pyrrole), 8.77 (d, 2H, β -pyrrole), 8.55 (d, 2H, H-2,6 phenyl), 8.32 (d, 6H, H-2,6 phenyl) 8.17–8.22 (d, 2H, H-3,5 phenyl), 7.50–7.58 (m, 6H, H-3,5 phenyl), 7.35–7.39 (m, 3H, H-phenyl), –2.77 (br s, 2H, internal-NH-pyrrole); UV-vis, THF (λ_{max} (log ϵ): 417.0(5.48), 513.0(4.21), 547.0(3.92), 590.5(3.76), 647.5(3.64). HPLC RT, min: 10.09 (eluting with acetone: toluene = 1:1, v/v); TLC (silica gel 60 Å, indicator F254, $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ = 3/1, v/v), R_f: 0.61; MS (ESI⁺): [C₄₅H₃₀N₄O₂] calcd for diprotonated porphyrin [M+2H]⁺ 717.68 g/mol; found 717.5 g/mol.

3. Results and discussion

3.1. The influence of pH on the UV-vis absorption spectra

The UV-vis spectra of the 5-(4-carboxy-phenyl)-10,15,20-tris(phenyl)-porphyrin were performed both for bare porphyrin in THF-water system (Fig. 2-right corner detail) and also by addition of acid, continuously changing the pH values (Fig. 2). The initial pH of the porphyrin solution in THF/water system is 5.5.

Porphyrins are recognized as photosensitizers because of their very strong absorption in the 400–450 nm region (Soret band) as well as absorptions in the 500–700 nm visible region (Q-bands). Those Q bands are numbered with IV–I, in accordance with the increasing of their wavelength position. The most red shifted is the QI band.

The UV-vis spectrum of bare-porphyrin displays *etio* type shape (absorption intensity continuously decreasing from QIV to QI band) with the maximum of the Soret band at 417 nm and the four Q-bands in the visible region, having maxima around 513, 547, 590.5 and 647.5 nm, respectively. The Soret band is due to the transition $a_{1u}(\pi) - e_g^*(\pi)$ and all the other QI–IV bands correspond to $a_{2u}(\pi) - e_g^*(\pi)$ transitions.

With increasing acidity from pH = 5.5 to pH = 1.5 (Fig. 2-main), two additional protons can be bonded to the nitrogen atoms in the porphyrin core. The generation of porphyrin dication determined important changes in UV-vis spectral allure. The most pregnant changes produced by increasing acidity are the splitting of the Soret band into two individual Lorentzian bands located around 417 nm and 445 nm respectively, accompanied by the continuously broadening of the Soret bands. This last mentioned feature is indicating some degree of J-type aggregation of the protonated species. Similar changes in UV-vis spectra due to variation of the ionic strength of acidic solution of porphyrins have been previously assigned to the formation of aggregates (Augulis et al., 2004).

The other changes are with respect to the QI band, which is forbidden otherwise, the UV-vis spectra show both an increase of the intensity and a significant bathochromic shift from 647 nm (pH = 5) to 665 nm (pH = 4).

The equilibrium between the monomer and the J aggregated protonated species is justified by the presence of the isosbestic point around 427 nm (Fig. 3). As can be seen in Fig. 3,

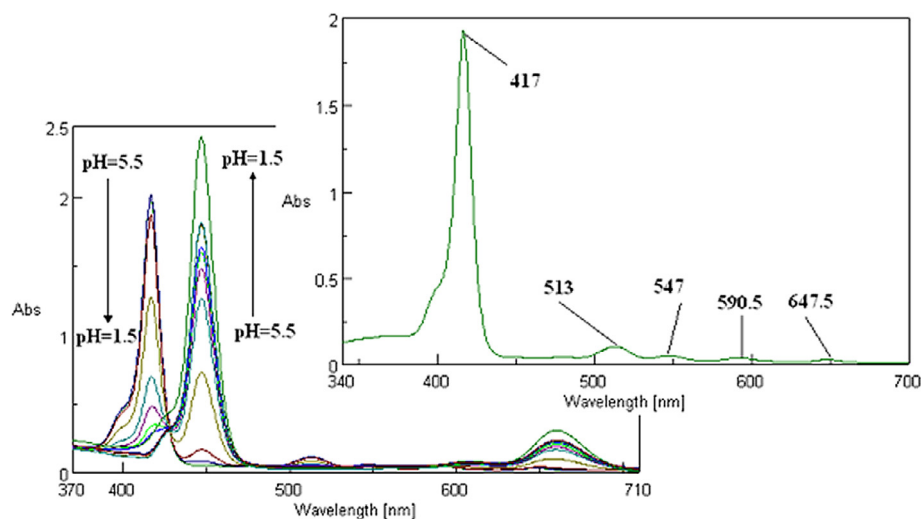


Figure 2 Dependence of UV-vis spectra of porphyrin upon addition of HCl (from pH = 5.5 to pH = 1.5) in THF-water solution; in detail the spectrum of porphyrin-base in non-acid THF-water system $C_{\text{porphyrin}} = 6.34 \times 10^{-6}$ M.

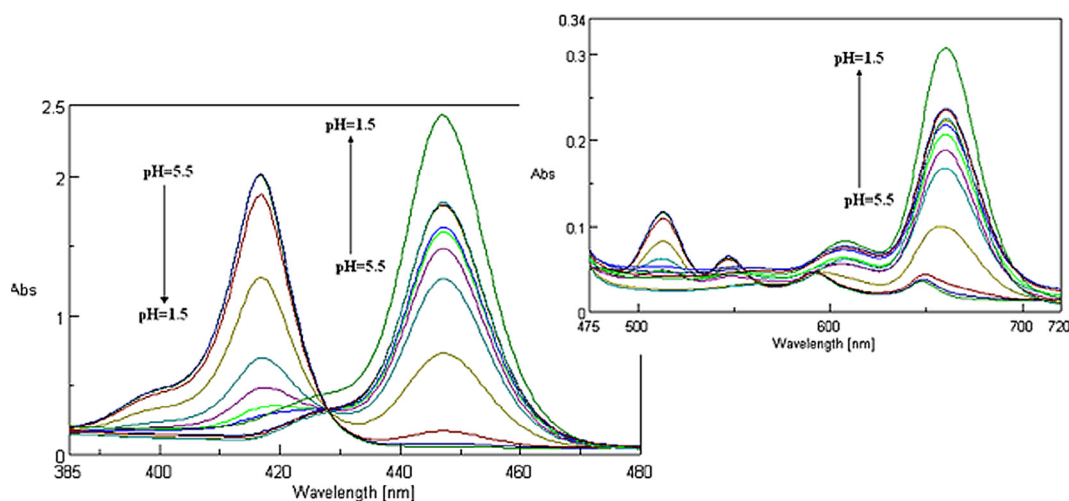


Figure 3 Equilibrium between monomer (417 nm) and J aggregated species (445 nm) in UV-vis spectra. Details of isosbestic point on Soret and magnified Q bands (right corner).

the protonated species coexist up to pH 2, but decreasing it to pH 1.5 solely the dicationic species are present.

Another major change is that, in acidic media, the Q bands are reducing to only one both hyperchromically and bathochromically shifted toward 665 nm. The decrease in the number of Q bands is due to an increase of symmetry to D_{4h} by protonation, and generation of the more symmetrical dication species (Fig. 3) (Fagadar-Cosma et al., 2007b).

3.2. The influence of pH on fluorescence spectra

The emission spectra of the porphyrin dye show two bands, assigned to $Q(0,0)$ and $Q(0,1)$ transitions, one of higher intensity around 653.5 nm, and a weaker one in the red region, at 718.4 nm, so that we can consider this porphyrin as belonging to *second generation photosensitizers* (it has also the capacity to absorb at long wavelength in the red region of the visible spectrum; $\lambda > 630$ nm).

The emission spectra of 5-(4-carboxy-phenyl)-10,15,20-tris(phenyl)-porphyrin performed at different acidic pH values in THF-water solution (1:1; v/v) are presented in Fig. 4.

The variation of pH was realized by adding 0.1–0.2 ml of HCl solutions of 0.001 M; 0.01 M; 0.02 M; 0.04 M; 0.06 M; 0.08 M; 0.1 M; 0.2 M; 0.4 M, 0.6 M; 0.8 M and 1 M, obtained from standard solution of 1 M, to 5 ml solution of porphyrin in THF/water 1/1 (v/v) system.

By continuously monitoring the variations in the main band intensity of the porphyrin emission spectra, induced by the exposure to different concentrations of acid, we noticed the linearity of the response at different pH values, in the acid range (Fig. 5), with a good correlation coefficient. A change in porphyrin color from red to emerald green was also noticed.

The emission spectra when pH is lower than 1.5 are represented in Fig. 6. Decreasing the pH of the porphyrin solution, produces a red shift of the $Q(0,0)$ band from 653 to 690 nm and the band $Q(0,1)$ is disappearing. The first phenomenon

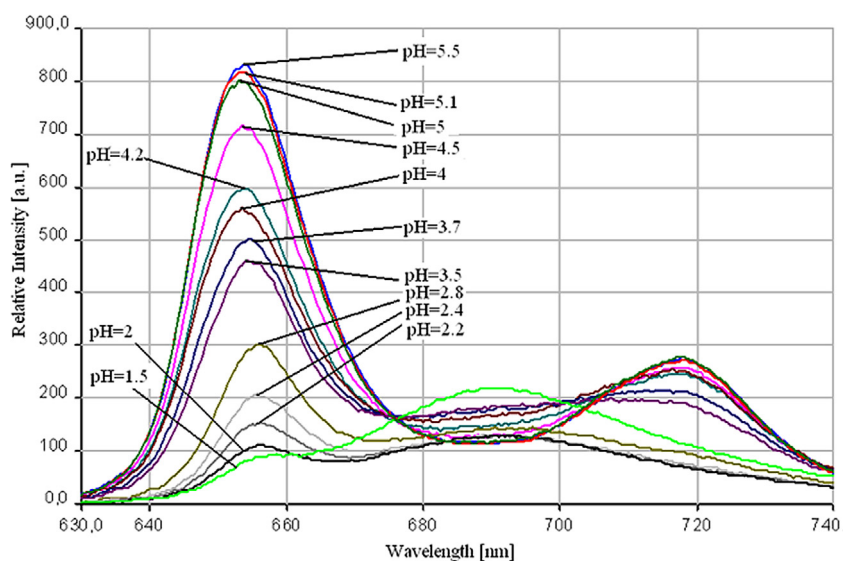


Figure 4 Dependence of the emission spectra of 5-(4-carboxy-phenyl)-10,15,20-tris(phenyl)-porphyrin performed at different acidic pH values (pH 1.5–5.5) in THF-water solution.

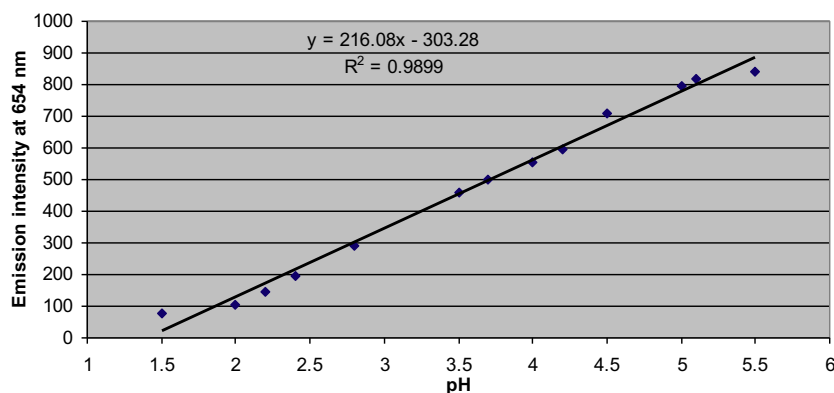


Figure 5 Dependence of the fluorescence intensity of the porphyrin function of pH variation.

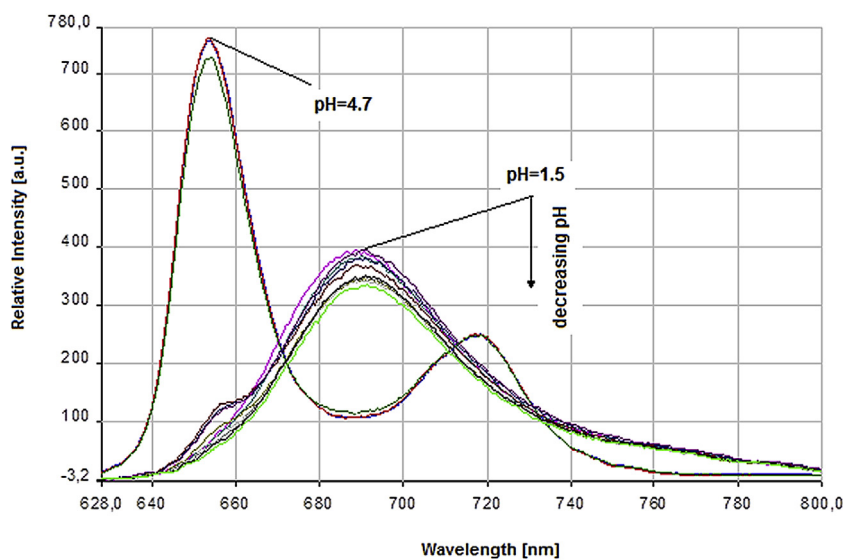


Figure 6 Comparison of the emission spectra of 5-(4-carboxy-phenyl)-10,15,20-tris(phenyl)-porphyrin performed at acid pH values and lower than pH 1.5, in THF-water solution.

after increasing of acidity lower than pH 1.5, shows the presence of the Q(0,0) band in the emission spectra as a pronounced shoulder on the novel bathochromically shifted band from 690 nm, but eventually, this is no more visible. So, the porphyrin is not suitable for measurements lower than pH = 1.5.

3.3. Selectivity

It must be checked if the proposed pH sensor revealed good selectivity toward a group of transition metal ions, because it is well known that the nitrogen donor atoms coordinate the transition metal ions to form metal complexes (Tutulea-Anastasiu et al., 2013).

Considering that inner nitrogen can bind in the porphyrin core various metal ions in solution, it is mandatory to determine whether other cations are potential interferences. A series of experiments conducted at pH 2.5, 3.5 and 4.5, consisting in addition of 1000-fold (molar) amounts of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , Co^{2+} , Mn^{2+} , Pb^{2+} , and Hg^{2+} , as chlorides, to the 5-(4-carboxy-phenyl)-10,15,20-tris(phenyl)-porphyrin solution, maintaining the other experimental condition unchanged, produced no changes regarding fluorescence intensity (Fig. 7).

Moreover, the influence of a mixture of metal cations similar to those existing in leaching solutions from Li-ion batteries recyclable processes upon the porphyrin emission spectra was checked (Fig. 7 illustrates the experiment at pH = 4.7). Synthetic leach liquors from spent lithium ion batteries, similar to the real ones (Granata et al., 2012), containing $1.36 \times 10^{-2} \text{ M Mn}^{2+}$, $8.48 \times 10^{-2} \text{ M Ni}^{2+}$, 1 M Li^+ , $3.56 \times 10^{-2} \text{ M Fe}^{3+}$, 0.17 M Co^{2+} and $4.7 \times 10^{-2} \text{ M Cu}^{2+}$

were prepared by weighting the appropriate amount of each salt in double distilled water.

This can be explained by the knowledge that metalloporphyrins cannot be generated into acidic media, so that 5-(4-carboxy-phenyl)-10,15,20-tris(phenyl)-porphyrin can accurately measure pH changes in the presence of various metal cations.

In basic media fluorescence is significantly quenched by the metal cations, so that there is no availability of the sensor for these environments.

4. Conclusions

A potential fluorescent pH sensor based on 5-(4-carboxy-phenyl)-10,15,20-tris(phenyl)-porphyrin as sensing agent has been presented. Upon increasing the acidity of the porphyrin solution the quenching of the fluorescence intensity was noticed, as a linear function of pH, with a good correlation coefficient.

Interference with various metal ions was tested to put into evidence the changes regarding the fluorescence intensity of the porphyrin, but the obtained results proved no significant changes on pH determination. The main conclusion is that 5-(4-carboxy-phenyl)-10,15,20-tris(phenyl)-porphyrin can measure pH in acid range in the presence of different metal ions making this sensor a proper one for pH determinations in leaching solutions of the recyclable processes of valuable metals.

Carbon nanotubes (CNTs) will be used to improve performance. Other approaches to improve the novel sensor will be performed by covalent immobilization of the dye into a hybrid sol-gel silica nanomaterial (Fagadar-Cosma et al., 2014) or an appropriate polymeric membrane.

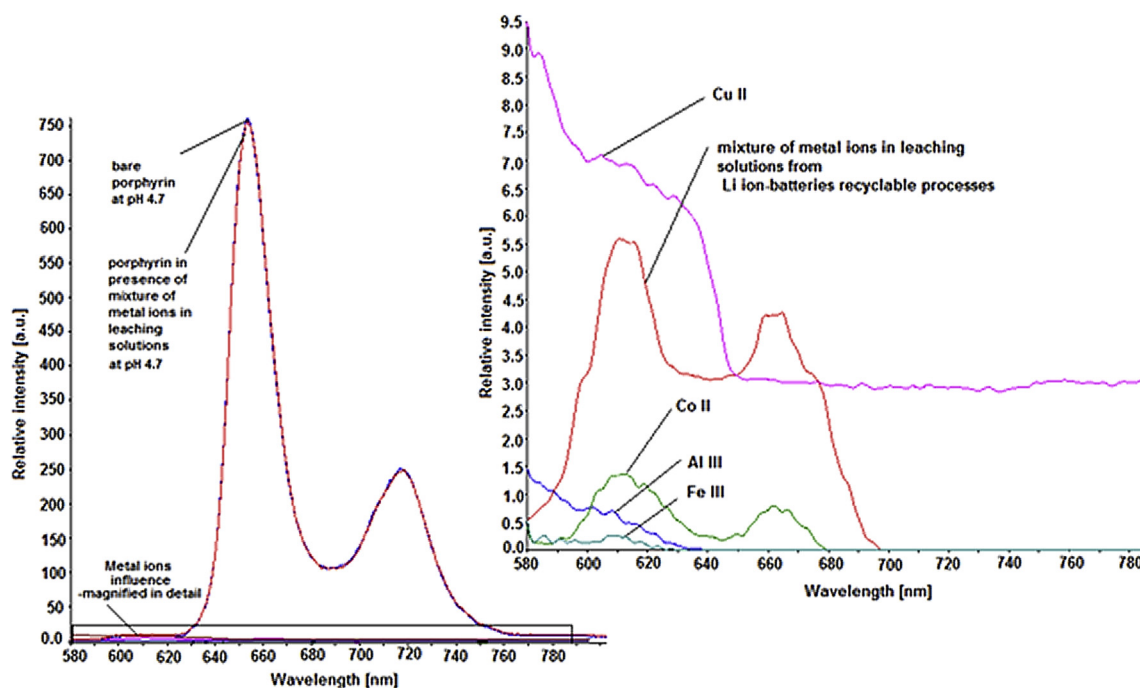


Figure 7 Comparison of the emission spectra of 5-(4-carboxy-phenyl)-10,15,20-tris(phenyl)-porphyrin performed at acid pH values, with and without metal cations. Detail: emission spectra of metal cations.

Acknowledgments

The authors are gratefully acknowledging European Community's Seventh Framework Programme (FP7/2007–2013) under Grant Agreement 266090 (SOMABAT), UEFISCDI Romanian co-financing EU-7FP-SOMBAT – Module III – No. 128 EU/2011, STAR-ROSA SAFEAIR-Project No. 76/2013 and Romanian Academy Programme No. 2/2013–2014 of Institute of Chemistry Timisoara.

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